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ASSESSMENT OF HEAVY METALS ALLOCATION AND CONTAMINATION INDICATOR IN THE SEDIMENTS OF COASTAL AREAS OF KARACHI, SINDH, PAKISTAN

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Abstract: Coastal areas of Karachi, Sindh, Pakistan were selected with the intention of study the accessibility of heavy metals and their concentrations in the surficial sediments (<60μm). These top soil samples were analyzed for Fe, Mn, Cr, Pb, Zn, Cu, Co, and As to scrutinize metals concentrations in sediments. Evaluation of anthropogenic pollution in sediments contamination indicator by Single-factor index analysis. Basic concentration of Mn is maximum in coastal sediments followed by Fe, Zn, Pb and As that is Mn > Fe > Zn > Pb > Co > Cu > As. This study exposed that confined geology has not revealed a few noteworthy influence on coastal sediments of the study area. The consequences of this study showed that Fe, Cr and As are the mainly severe pollutants in creek / beach sediments especially at Port Qasim industrial area i.e. (average 1104, 31 & 1.9 ppm) and Ketti Bunder i.e. (average 45, 0.67 & 5.03 ppm).

Key words: heavy metals, contamination, sediments, coastal area, pollutants

1. INTRODUCTION

Soil is not only a medium for plants to grow or a pool to dispose of undesirable materials, but also a source of many pollutants to surface, ground and coastal water. So the accumulated pollutants in surface soils ultimately transported to different environmental components of coastal aquifers. Soil analysis offers advantages over water analysis for the control and detection of metal pollution in estuaries (Förstner & Wittman, 1983), although metal concentrations may also fluctuate over time (Araujo et al., 1988).

Heavy elements found in soils/sediments are immobilized in water and thus could be involved in absorption, co-precipitation, and complex formation (Okafor & Opuene, 2007). Sometimes they are co-adsorbed with other elements as oxides, hydroxides of Fe, Mn, or may occur in particulate form (Awofolu et al., 2005). Their concentrations in stream and coastal sediment compartments can be used to reveal the history and intensity of local and regional pollution (Nayangababo et al., 2005).

Anthropogenic activities have greatly altered the geochemical cycle of heavy metals, resulting in widespread environmental contamination (Nriagu & Pacyna, 1988). The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon mineralogical composition and depositional environment of the sediments (Trefry & Parsley, 1976).

The coastal areas of Sindh at the northern part of the Arabian Sea and specially the beaches of Karachi belong to the best beaches in the world. The beaches of Karachi were formed by the Hub River in the west and the Indus River in the east. The coast of Karachi can be divided into two parts; one lying on the west from the navigation channel of Karachi harbor, starting from Manora Island extending up to Cape Monze and ultimately to Makran coast beginning from Gadani beaches. The other part of the coastline is on the eastern side on navigation channel, which comprises of Clifton, Gizri and Ibrahim Haidari beaches. Discharge of toxic chemicals, over pumping of aquifer and contamination of water bodies with substance that promote algae growth are some of the today's major cause for water quality degradation

It has been observed worldwide that the impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to the study areas (Nouri et al., 2008), as the coastal area receives significant amount of waste containing metal from municipal wastewater, garbage and industrial effluents. In the study area, heavy metals enter into aquatic ecosystems mainly from anthropogenic sources, such as industrial wastewater discharges, sewage wastewater and fossil fuel combustion (Linnik & Zubenko, 2000).

The collection of soil samples for trace metals in the study area has been done to serve a basis for the planning of control strategies to achieve better environmental quality, and will as a key for an effective management of soil quality; similar extensive investigations of coastal soils have been carried out recently in many countries (Weiss et al., 1994). These soil samples were analyzed for Fe, Mn, Cr, Pb, Zn, Cu, Co and As to examine metal concentrations in sediment. Therefore, the study will attempt to evaluate the extent of heavy metal contamination from the surface to the bottom sediments and the degree to which heavy metals are influenced. The spatial distribution and the transportation procession of trace element in surficial sediments were studied to illustrate distinct pattern of the functional area and were plotted by Golden Software's SURFER program. The q-q plot made by SPSS, the single-factor model.

2 MATERIAL AND METHODS

A total 21 samples of coastal sediments from different locations of Karachi, Sindh were collected during 2012- 2013 (Fig. 1; Table 1).

The inference of the entire metals concentration, from sediments was determined according to (Williams et al., 1994). Sediment samples were taken from depth of 0-20 cm which was promptly crammed in air fixed plastic bottles. Sub-samples of the material were oven dried at 500 °C for 48 hours and ground using mortar and pestle. Then the samples were sieved by <63 μm sieving net and 2 gm of sub sediment sample were digested by using acids mixtures (HNO_3 + $HClO_4$ + HF) correspondingly, to acquire the total concentration of the metals in the sediments has been suggested by (Araujo et al., 1988). Safety measures were taken to avoid contamination throughout drying, grinding and sieving. Co, Ni and Pb concentrations were determined with Atomic Absorption Spectrophotometer. All furnace measurements were performed using an Agilent 280Z AA spectrometer fitted with an Agilent PSD 120 Programmable Sample Dispenser. For the single index factor analysis the mathematical expression is written as follows:

$$Pij = Cij / Sj$$

Where *Pij* is the pollution index of the heavy metal *j* in the *i*-th functional area soil. *Cij* is the measured contamination value of heavy metal *j* in the *i* -th functional area soil, and *Sj* is the background contamination value of heavy metal *j*.

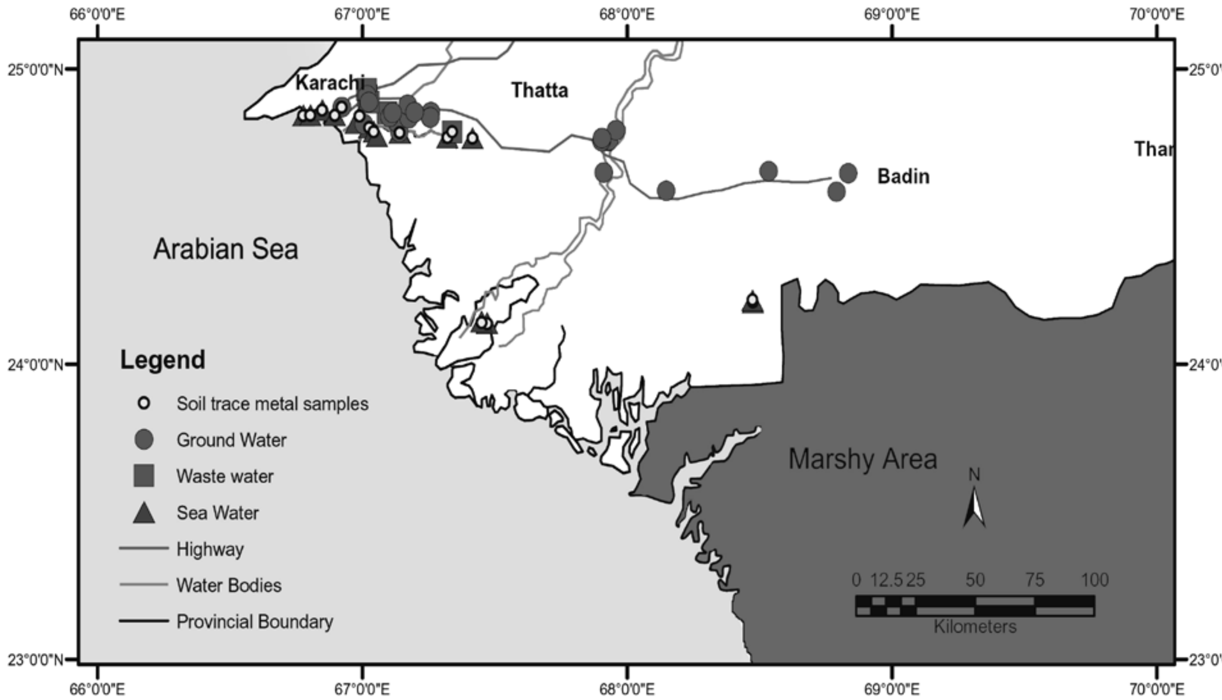


Figure 1. Map of the study area.

Table 1. Soil analysis results of coastal sediments from different locations of Karachi, Sindh.

Name of locations	X	Y	Cr	Cu	Fe	Mn	Pb	Co	Zn	As
			ppm							
Qazi Muhammad, 1Runn of Kutch	68°47'4.26"E	24°21'0.15"N	0	0	9.2	84	5	0	48	0.002
Qazi Muhammad, 2Runn of Kutch	67°11'5.43"E	24°55'2.46"N	0	0	11.7	77	8	0	51	0.001
Main keti Bandar (East)	67°27'9.47"E	24° 8'20.63"N	0.3	0.9	56	57	2	4.5	24	4.7
Keti bandar 1	67°27'9.59"E	24°8'0.43"N	1	1.1	38	48	2	4.3	18	6.1
Keti bandar 2	67°27'6.97"E	24°7'.78"N	0.7	0	43	52	0	4.2	22	4.3
Port Qasim JT	67°34'8.22"E	24°7'7.58"N	34	3	1130	433	37	6.9	213	2.1
Steel mill, Bin Qasim	67°33'9.03"E	24°78'7.37"N	28	2.6	1078	321	36	7.7	161	1.7
Mazar Russian Beach, Back side of Steel Mill, Bin Qasim	67°3'9.91"E	24°78'7.63"N	24	2.1	876	378	28	5.8	195	0.9
Ibraheem Hyderi Korangi	67°14'0.41"E	24°78'4.84"N	35	3.6	374	912	29	8.5	151	0.04
Sea View, Hyper Star Building, Clifton	67°02'7.72"E	24°80'3.22"N	0.7	0.6	37	718	11	11.1	81	0.035
Sea View, Floating Ship, Clifton	67°0'4.47"E	24°78'9.71"N	0.9	0.7	34	688	13	12.4	76	0.055
Main Manora	66°58'11.15"E	24°48'13.99"N	26	2.3	24	349	18	12.7	587	0.06
Manora beach 1	66°58'17.29"E	24°47'48.93"N	28	2.8	27.7	356	22	13.7	543	0.05
Manora beach 2	66°56'41.81"E	24°48'56.98"N	25	2.5	26.1	330	19	12.9	564	0.02
Native Jeti Bridge, Left Side, Kemari	66°98'3.42"E	24°8'3.36"N	16	2.7	28	366	26	17.9	598	0.07
Main Sandspit	66°55'23.30"E	24°49'57.74"N	8	2.7	19.8	418	14	14.2	56	0.004
Main Hawks bay	66°52'26.79"E	24°51'22.07"N	6	5	33	385	16	14.8	53	0.012
Hawaks Bay 1	66°50'54.48"E	24°51'40.73"N	4	2.8	34	417	17	15.8	65	0.003
Hawaks Bay 2	66°89'7.76"E	24°84'5.01"N	7	2.5	32	410	18	16.6	61	0.002
Paradise Point 1	66°77'5.79"E	24°84'5.51"N	5	2.9	42	389	16	12.4	54	0.43
Paradise Point 2	66°80'9.69"E	24°84'5.73"N	4	2.4	47	475	15	12.8	49	0.24

3 RESULTS AND DISCUSSIONS

3.1 Allocation of heavy metals concentration

In this study area, heavy metals allocation in the coastal sediments exhibits three trends. Highest values were detected in the deepest area near to Ketti Bundar, in the background of port Bin Qasim and in the axial areas. Most important elements (Fe, Mn, Cr, Cu, Pb, Zn and As) best imitate these trends (Fig. 2a - e, g, h). Iron and Mn contents have a peak at station no. 8 and 5 in the transect between Ketti Bundar and port Bin Qasim (Fig. 2a, b). In contrast, the allocation model of the majority of the heavy elements follows only one or two of these trends. For instance Cr and Zn showed highest values towards south east and south west part of the study area (Fig. 2 c, g). Copper, Pb and Co are circulated in different way (Fig. 2 d, e, f) with the prohibiting that allocation pattern of Cu showing ordinary pattern with both Pb and Co. While Mn and As have shown fairly similar allocation pattern (Fig.2 b, h) as both of these element are concentrated in the south east region of the study area at station no. 7, 8 and 9.

The Fe content showed a very elevated value in the internal part of the port Bin Qasim (1130, 1078 and 876 ppm), but, excluding these value, mean values are approximately 190 ppm (see Fig. 2a). While the Mn maximum concentrations (912, 718 and 688 ppm) are placed at coastal belt of Karachi (i.e., Ibrahim Hyderi, Hyper star building and Floating ship) corresponding to sandy areas (see Fig. 2b). It is predictable that in the study area the presence of Mn surrounded by the calcite in the sediments indicates the elevated deliberation of these sediments under toxic conditions. The allocation pattern of Mn discovered that the coastal area of Karachi has highly elevated in Mn concentration (Fig. 2b). So, the elevated concentration of Mn is found in Karachi due to origin of the marine environment.

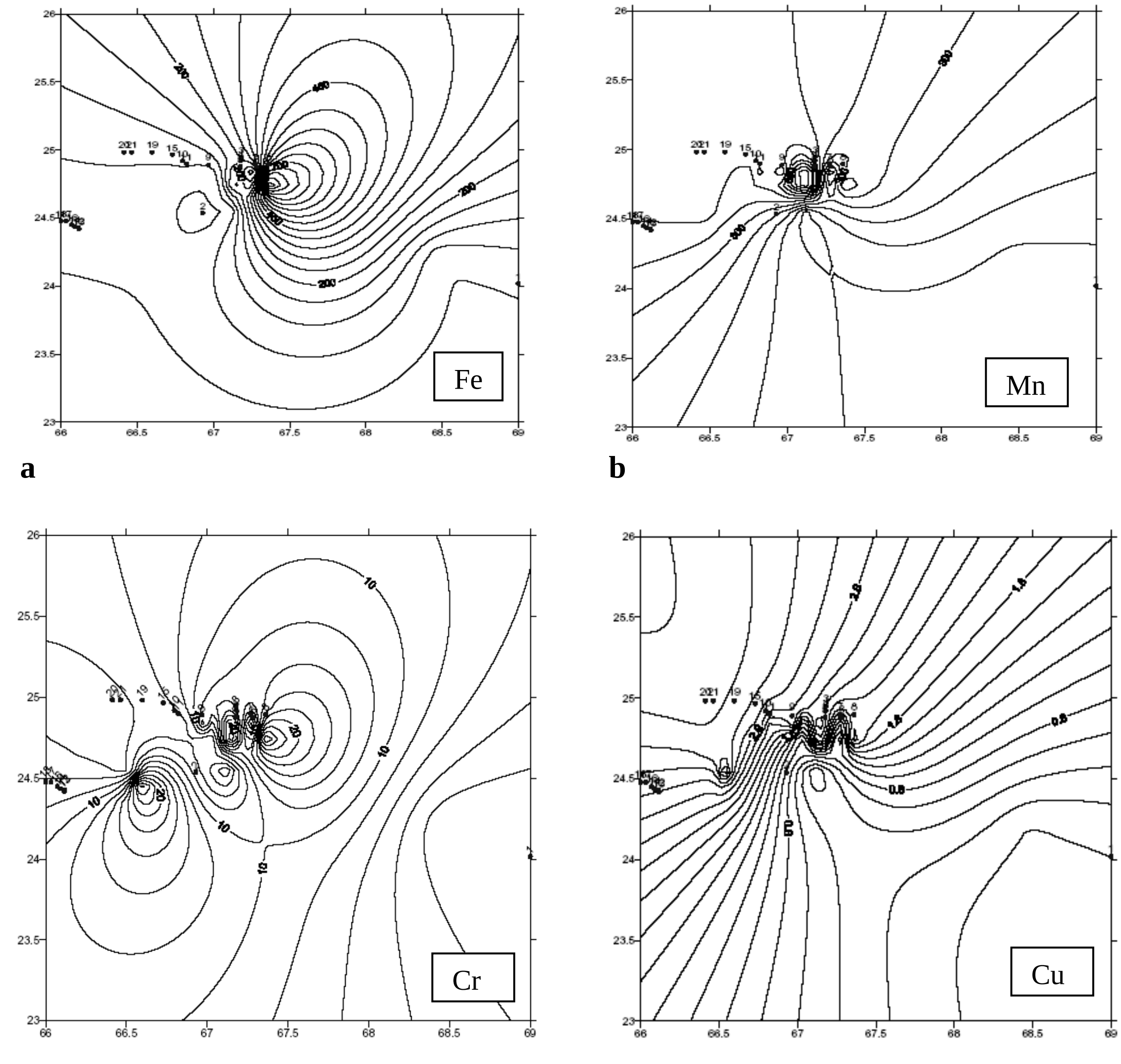
The contour pattern of Cr showed high values at Ibrahim Hyderi (35 ppm) (Fig. 2c). However, at only some locations samples have a little noticeable Cr contents. The irregular allocation of Cr is recognized to its incidence due to release of industrial waste water release into stream and coastal sediments.

Copper has similar allocation pattern (Fig. 2d) as of Co and Pb. The incidence of Pb content showed a high value in the inner part of the port Bin Qasim (37 and 36 ppm), but, not including these value, mean values are approximately 17.6 ppm (Fig. 2e). This might be attributed to release of Pb adsorption by marine sediments. The high concentration of Pb may be due to its release from dead or decay marine organisms and / or through precipitation. There is slight proof that Pb is readily missing from soil profiles by leaching. The majority of heavy metals, including Pb, remain in an insoluble or stable form in surface layers of sediments after application of sewage sludge. So it can be assume that in the study area the source would be geogenic from the run of sediments.

By distinction, Co content (Fig. 2 f) shows high values (17.9 ppm) in Kemari (Native Jetty) with a minimum at Ketti Bunder (4.2 ppm). In the study area, Co tends to be co-precipitated with Fe oxides and particularly with Mn oxides.

Allocation pattern of Zn also showed the high trends in stations located in south west site of coastal area i.e., Kemari and Manora harbor (598 and 587 ppm) (Fig. 2 g), but, apart from these value, mean values are approximately 174 ppm. These stations were most likely exaggerated by industrial dissipate.

Arsenic showed high value at Ketti Bunder (6.1 ppm) (Fig. 2h). In numerous locations concentration of this element has below 0.001 ppm. This element has very low measurable values in all samples. In the study area the occurrence of As is associated with sedimentary rocks of marine origin, fossil fuels, industrial wastes, agricultural use, and irrigation practices.



a b c d

Figure 2 (a, b, c, d). Allocation pattern of Fe, Mn, Cr & Cu in soil sediments of coastal aquifers.

High concentrations of heavy metals are found in stations located in south eastern part or in the central region of the study area. This result may be due to decrease water current in these parts that causes reduce chemical interactions between metals and sediment such as: suspended solid absorption, surface sediment sorption and rate of re-deposition which is dependable an augment metals concentration.

Number of researchers reported that silt and clay in sediment play significant role in deposition and entrapment of pollutants during adsorption process (Nobi et al., 2010). Zn and Cr also showed the high trends in stations located in south east site of coastal area; these stations were probably affected by industrial waste which is loaded from the industrial outlets that were located along coastline. The content of As, Zn and Pb decreased from mangrove line to coastlines.

The concentration of As, Zn and Pb are significant at Ketti Bunder, Kemari and port Bin Qasim because these stations are influenced both the mangrove sedimentation and industrial waste which is loading from coastline. Several researchers suggested that sediment of mangrove forests act as trap for chemical contaminates because their sediment contain high percentage of silt and clay that increase metals adsorption in these stations (Vallejuela et al., 2010). This is also true in our study area.

The distribution pattern of these metals showed that the fine-grained sediments are concentrated at the mouth of the estuary and near the shore of the coastal area, where the hotspots of trace metals are situated (Fig. 2a, b, c, d & e).

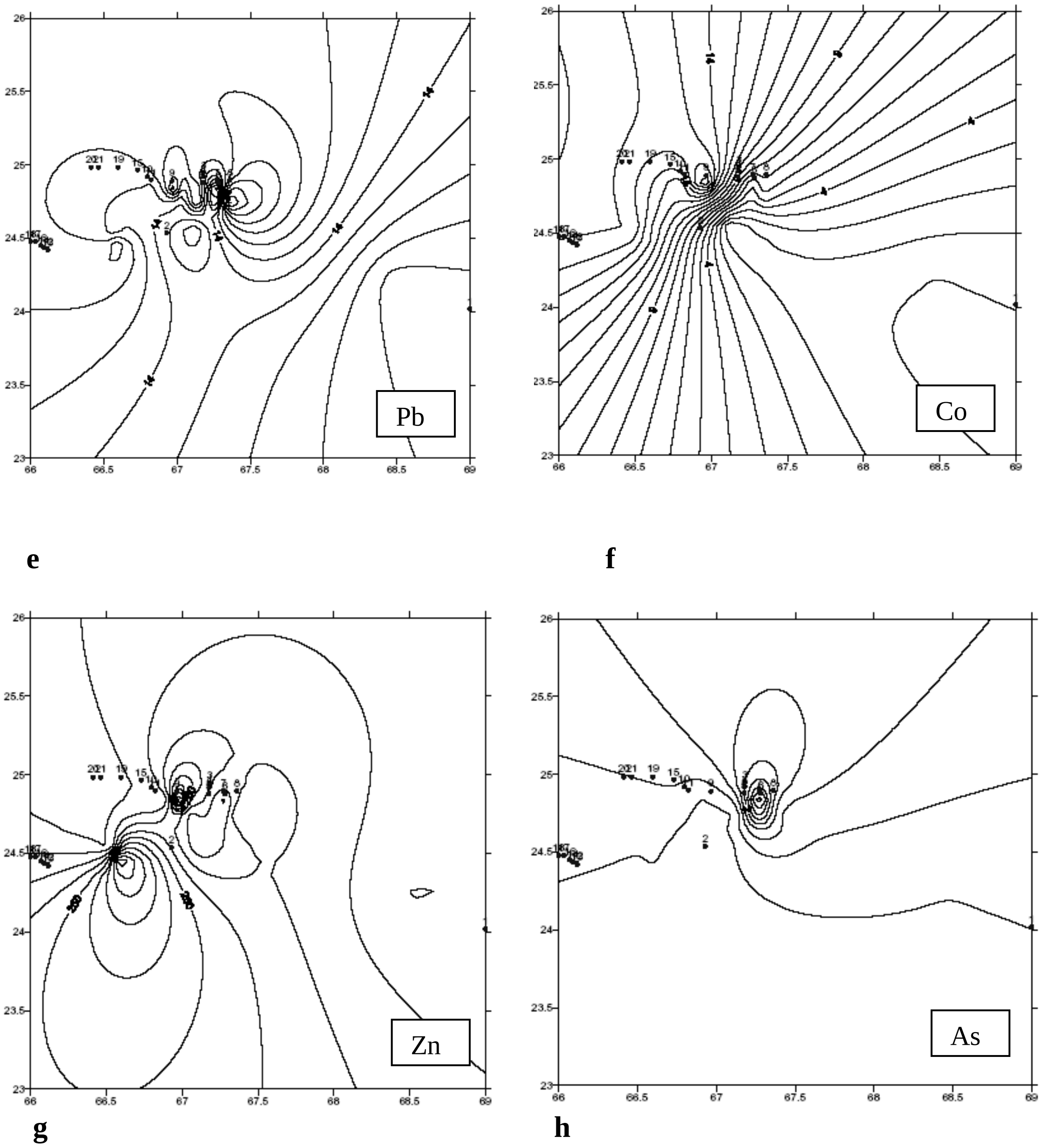


Figure 2 (e, f, g, h): Allocation pattern of Pb, Co, Zn & As in soil sediments of coastal aquifers.

This indicated that fine particles might be a major carrier for transporting trace metals from the upstream source area to the coastal zone. The grain size of sediments is a reflection of the hydrodynamic processes and the deposition conditions in a coastal region (Zubair, 1993).

From this study it infers that the physical properties (e.g. grain size) of sediments may affect the concentration of trace metals in estuaries and coastal areas. In the study area within estuarine, the clay content of the sediments increases in the direction of the sea. On the other hand, at the coastal area, the clay content of the sediments decreases along the direction of the ocean (Lin et al., 2002). This pattern reflects a typical sediment transport mechanism in river delta regions (Chen et al., 1999), and this is in agreement with the numerical modelling of the transport of sediments by tidal currents (Williams et al., 1994). This demonstrates that the sediment transported into the estuarine is mainly accumulated from the Indus river outlets.

Therefore it can be say that physical transportation is not the only way to control the pattern of trace metals in the estuary and coastal mixing zone. It is also the most important factors to control the spatial variations of the trace metals in sediments included grain size and chemical conditions (e.g. sorption, adsorption of trace metals, flocculation, etc.) of the sedimentary environment and anthropogenic pollution (Williams et al., 1994). So, in the study area, the distribution of trace metals between solution and particulate materials is strongly affected by the changes in the chemical property of particles in estuaries and their surroundings of coastal area.

Elemental concentration of Mn is highest in coastal sediments followed by Fe, Zn, Pb and As i.e. Mn > Fe > Zn > Pb > Co > Cu > As. The sediments from industrial discharge sites have the highest concentrations of Fe, Mn and Zn. Mean Pb concentration is highest in port Bin Qasim and Steel Mill wastewater discharge point.

This study also revealed that local geology has not shown any significant influence on coastal sediments of the study area. This is due to alluvial deposits of sand, silt, gravel and clay where the large numbers of open water tables aquifers occurs; there is no effect of geology in the chemical composition of coastal aquifers of the study area. Furthermore the hydrological pathways of these aquifers also demonstrate that the coastal aquifers of the study area are not influenced by the local geology.

3.2. Heavy metals contamination

The most important reason of sediment quality guidelines (SQGs) are to protect aquatic biota from the harmful and toxic effects related with sediment bound contaminants and is a useful tool for evaluating potential for contaminants within sediment to persuade biological effects.

3.3. Single-factor index analysis

The single factor index evaluation method is engaged to get actual quantitative information of key contamination elements and excessive multiples, which is one of the most existing methods used in evaluation of the degree of heavy contamination in soil. Heavy metal contaminants Fe, Mn, Cr, Cu, Pb, Co, Zn and As are numbered as 1 to 8, respectively.

According to the value of P_{ij}, this can be determine which kind of pollutants exceeds and the excessive multiple in different area in the coastal belt of the province, and additional determine what are the most serious pollutants and most serious regions of the pollution. According to the related information, the grading standard of single-factor is shown in table 3.

The pollution indexes of the heavy metals in each region are calculated and shown in table 3, respectively. The results of this study showed that Fe, Cr and As are the most serious pollutants in creek / beach sediments especially at Port Bin Qasim industrial area and Ketti Bunder, where the pollution index of these metals are relatively high as the usual value (Table 3).

Table. 2. The evaluation grading standards of the single factor index method

Sub -Index	$P_{ij<1}$	$1 \leq P_{ij} < 2$	$2 \leq P_{ij} \leq 3$	$3 \leq P_{ij}$
Quality grade	clean	Potential Pollution	Slight pollution	Heavy pollution

Table 3. Pollution index of each heavy metal in the study area

Heavy metals (mg^{-l})	Cr	Cu	Fe	Mn	Pb	Co	Zn	As
Contaminated value (C_{1j})	0.3	0.9	56	57	2	4.5	24	4.7
Background V value (Sj)	0.3	0.9	9.2	48	2	4.2	18	1.7
Pollution Index (P_{1j})	1	1	6.1	1.2	1	1.1	1.3	3
Quality grade	Clean	Clean	Heavy pollution	Potential pollution	Clean	Potential pollution	Potential pollution	Heavy pollution

The observable fact indicates that there are many factories in the industrial areas of Port Bin Qasim and Landi. The results of the study further demonstrates that heavy metal pollution index, showing a state of potential contamination with respect to chromium where municipal and industrial waste received from Korangi and Landi industrial areas are discharging their waste at fishing harbor. While the samples collected from beach at Paradise point, Hawksbay and Ketti Bunder (close to creek) have not shown any noteworthy impact with respect to other heavy metals excluding Arsenic which is due to accumulation of vertebrate animal in sea sediment.

4 CONCLUSIONS

Except Cu, Co, As and Mn, most of the metals showed different patterns. High concentrations of heavy metals are found in stations located in SE part or in the central region of the study area. This result may be due to decrease water stream in these parts that causes reduce chemical interactions between metals and sediment. This study also revealed that local geology has not shown any major influence on coastal sediments of the study area. This is due to alluvial deposits of sand, silt, gravel and clay where the large numbers of unconfined aquifers occur **s**amples collected from Paradise point, Hawksbay and Ketti Bunder (close to creek) have not shown any significant impact with respect to other heavy metals except of As. The results of this study showed that Fe, Cr and As are the most serious pollutants in creek/ beach sediments especially at Port Bin Qasim industrial area and Ketti Bunder where the pollution index of these metals are relatively high as the normal value.

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REFERENCES

Araújo, M.F.D., Bernard, P.C. & Van Grieken R.E.,1988 *Heavy metal contamination in sediments from the Belgian coast and Scheldt estuary.* Mar. Pollut. Bull., 19 (6), 269–273.

Awofolu, O.R., Mbolekwa, Z., Mtshemla, V. & Fatoki, O.S., 2005. *Levels of trace metals in water and sediments from Tyume River and its effects on an irrigated farmland.* Water SA, 31 (1), 87-94.

Chen, Y., Wai, O.W.H. & Li, Y.S.L.Q. 1999. *Three-dimensional numerical modeling of cohesive sediment transport by tidal current in Pearl River Estuary*. International Journal of Sediment Research 14, 107e123.

Förstner, U. & Wittman, G.T.W., 1983. *Metal Pollution in the Aquatic Environment*. Springer Heidelberg., 486 p.

Lin, S., Hsieh, I.J., Huang, K.M. & Wang, C.H., 2002. *Influence of the Yangtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China Sea continental shelf sediments.* Chemical Geology 182, 377e394.

Linnik, P.M. & Zubenko, I.B., 2000. *Role of bottom sediments in the secondary pollution of aquatic environments by heavy metal compounds,* lakes and reservoirs. Res. Manage., 5 (1), 11 – 21.

Nobi, E.P., Dilipan, E., Thangaradjou, T., Sivakumar, K., & Kannan, L., 2010. *Geochemical and geo-statistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India.* Estuarine, Coastal and Shelf Science. 87(2): 253-264.

Nouri, J., Karbassi, A.R, & Mirkia, S., 2008. *Environmental management of coastal regions in the Caspian Sea.* Int. J. Environ. Sci. Tech., 5 (1), 43-52.

Nriagu, J.O. & Pacyna, J., 1988. *Quantitative Assessment of Worldwide Contamination of Air, Water and Soil by Trace Metals,* Nature, 333: 134-139.

Nyangababo, J.T., Henry, E. & Omutange, E., 2005. *Lead, cadmium, copper, manganese and zinc in wetland waters of Victoria Lake Basin, East Africa.* Bull. Environ. Contam. Toxicol., 74 (5), 1003-1010.

Okafor, E.C.h. & Opuene, K., 2007. *Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments.* Int. J. Environ. Sci. Tech., 4 (2), 233-240.

Trefry, L.H. & Parsley, B.J., 1976. *Heavy metal transport from the Mississippi river to the Gulf of Mexico. In: HL Windhom and R. A Duce (Eds.).* Marine Pollution Transfer. Lexington: Lexington Books, pp. 39-76.

Vallejuelo, S.F.O., Arana, G., Alberto, D. & Juan, M. M., 2010. *Risk assessment of trace elements in sediments: The case of the estuary of the Nerbioi–Ibaizabal River (Basque Country).* Journal of Hazardous Materials (181):565-573.

Weiss, P., Riss, A., Gschmeidler, E. & Schentz, H., 1994. *Investigation of heavy metal, PAH, PCB patterns and PCDD/F profiles of soil samples from an industrialized urban area (Linz, upper Austria) with multivariate statisti- cal methods.* Chemosphere 29(9-11), 2223-2236.

Williams, T.P., Bubb, J.M. & Lester, J.N, 1994. *Metal accumulation within saltmarsh environments*: a review. Marine Pollution Bulletin. 28:277-29.

Zubair, A. 1993. *Ocurrence and properties of aquifier in Northern Karachi, M.Phil thesis.* Department of Geology, University of Karachi, Pakistan, p. 7-13 & 26.

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